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Feasibility of Using Solid Adsorbents for Dioxin Sampling

Battelle Columbus Labs., OH

Prepared for

Industrial Environmental Research Lab.
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FEASIBILITY OF USING SOLID ADSORBENTS FOR DIOXIN SAMPLING

by

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16. ABSTRACT The report gives results of a determination of the recovery efficiencies from XAD-2 resin (Amberlite) and Florisil of spiked 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), in order to assess the suitability of these adsorbents for sampling. Two spiking methods were used: Method A consisted of uniformly depositing 1 mL of the spiking solution onto the adsorbent, and Method B consisted of covering the whole adsorbent sample with the spiking solution. There was no significant difference in recovery efficiencies between the two methods or between the two adsorbents. Overall recovery from XAD-2 resin was 92 +/- 8%, and 95 +/- 6% from Florisil.

17. KEY WORDS AND DOCUMENT ANALYSIS

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Pollution Analyzing	Pollution Control	13B
Heterocyclic Compounds	Stationary Sources	07C
Hydrocarbons	Dioxins	
Adsorbents	Tetrachlorodibenzo-p-dioxin (TCDD)	11G
Combustion		21B
Sampling		14B

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NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

The recovery efficiencies from Amberlite® XAD-2 resin and Florisil® of spiked 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) were determined in order to assess the suitability of these adsorbents for sampling. Two spiking methods were used: Method A consisted of uniformly depositing 1 mL of the spiking solution onto the adsorbent, and Method B consisted of covering the whole adsorbent sample with the spiking solution. No significant difference in recovery efficiencies was found between the two methods or between the two adsorbents under study. The overall percent recovery from Amberlite® XAD-2 resin was 92 $\pm$ 8 and from Florisil®, 95 $\pm$ 6.

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SECTION 1

INTRODUCTION

Due to the well known toxicity and ubiquitous nature of polychlorinated dibenzo-p-dioxins (PCDDs) they are the subject of great interest in determining their route of entry into the environment. Although PCDDs are known to be formed during certain industrial chemical manufacturing processes (e.g., polychlorophenols and their derivatives), it is suspected that combustion sources may be the major source of environmental loading. In order to determine the presence of trace quantities of this class of compounds (in combustion gas streams), 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) was chosen as a test case. Two programs were initiated by the U.S. Environmental Protection Agency in order to demonstrate the reliability of the sampling and analysis procedures.

This program which was aimed at assessing the extraction efficiency of 2,3,7,8-TCDD from Amberlite® XAD-2 or Florisil®, the adsorbents normally used in collecting organics emitted from combustion sources in either the Source Assessment Sampling System (SASS) train or the Modified Method 5 (MM5). The other program conducted under Task 131, Contract Number 68-02-2686, focused on determining the recovery efficiency of a continuous, dynamic calibration spike of 2,3,7,8-TCDD directly in the emission of an operating combustion system using either the SASS or MM5 sampling trains.

The data obtained from these two studies demonstrated the efficiency of dioxin recovery in the sampling system as a whole and in adsorbent material that constitutes the collection medium of the TCDD in particular.

SECTION 2

CONCLUSIONS

- No significant difference was observed in spike recoveries whether spiking Method A where 1 ml aliquot of the spike solution was deposited on the adsorbent or Method B where 25 ml of the spiking solution covered the whole adsorbent sample was used. However, Method B appears to be slightly more representative of how TCDD will be distributed and adsorbed on the surface of the actual sample.

  The average percent recovery of spiked 2,3,7,8-TCDD from XAD-2 at 2.1 ng and 16.5 ng levels was 94 $\pm$ 6 when Method A was used and 91 $\pm$ 10 when Method B was used.

  The average percent recovery of spiked 2,3,7,8-TCDD at 2.1 ng and 16.5 ng levels from Florisil was 102 $\pm$ 6 when Method A was used and 89 $\pm$ 6 when Method B was used.

- The overall average percent recovery of 2,3,7,8-TCDD in all of the experiments performed with XAD-2 was 92 $\pm$ 8. This number is comparable with the overall average recovery of 94% obtained for the whole system as described in Task 131, Contract Number 68-02-2686.

- No significant difference in recovery efficiencies of 2,3,7,8-TCDD from either XAD-2 or Florisil was observed. However, XAD-2 has the advantage of being a more universal adsorbent for organics in general.

SECTION 3

EXPERIMENTAL

The spiking of 2,3,7,8-TCDD into Amberlite® XAD-2 and Florisil® was carried out using two Methods, A and B.

METHOD A

This method consisted of uniformly depositing 1 mL of methylene chloride containing either 3 ng or 30 ng of 2,3,7,8-TCDD onto the surface of a 15 g portion of the adsorbent. This method is not expected to result in a uniform distribution on the adsorbent.

METHOD B

This method consisted of depositing ~25 mL of the methylene chloride spiking solution to cover the whole body of the adsorbent. The spiking, therefore, was uniform onto the adsorbent. The methylene chloride was removed by evaporation at room temperature for both methods.

A summary of the experiments performed and the spike levels is given in Table 1.

SAMPLE EXTRACTION AND CLEANUP

Each of the adsorbent samples, spiked with 2,3,7,8-TCDD using either Method A or Method B, was Soxhlet extracted for 16 hours with 250 mL of methylene chloride. The methylene chloride extract was spiked with 2 ng of 2,3,7,8-TCDD-$^{13}C_{12}$ to serve as an internal standard for quantification of native 2,3,7,8-TCDD and to correct for any losses which occurred during the clean-up and concentration of the extracts.

The methylene chloride extracts were quantitatively transferred to Kuderna-Danish (K-D) concentrators using three 10 mL rinses of fresh methylene chloride and concentrated to approximately 1 mL.

The extracts were cleaned up by passing them through a series of gravity fed liquid chromatography columns. The first column was a multilayered silica column containing alternate layers of activated silica, 44% concentrated sulfuric acid on silica and 33% 1M potassium hydroxide on silica. This column is schematically illustrated in Figure 1. The concentrated methylene chloride extract was transferred to the column using three 5 mL rinses of hexane. The

TABLE 1. SUMMARY OF PERFORMED EXPERIMENTS

Adsorbent	Spiking Method	Number of Replicate(s)	2,3,7,8-TCDD Spike (ng/15 g)[a]	2,3,7,8-TCDD Level (ng/m^3)[b]
XAD-2	A	1	0	0
XAD-2	A	3	2.1[c]	0.7
XAD-2	A	3	16.5[c]	5.5
XAD-2	B	1	0	0
XAD-2	B	3	2.1[c]	0.7
XAD-2	B	3	16.5[c]	5.5
Florisil	A	1	0	0
Florisil	A	3	2.1[c]	0.7
Florisil	A	3	16.5[c]	5.5
Florisil	B	1	0	0
Florisil	B	3	2.1[c]	0.7
Florisil	B	3	16.5[c]	5.5
TOTAL NUMBER OF TESTS:		28		

(a) 150 g XAD-2 or Florisil is the standard amount used in a SASS train adsorbent cartridge. This quantity was scaled to 15 gm (10%) in order to minimize the use of 2,3,7,8-TCDD.

(b) Based on 30 m^3 total stack gas emissions for a standard SASS train run.

(c) These are the actual levels obtained when the spiked solutions targeted at 3 ng and 30 ng were analyzed.

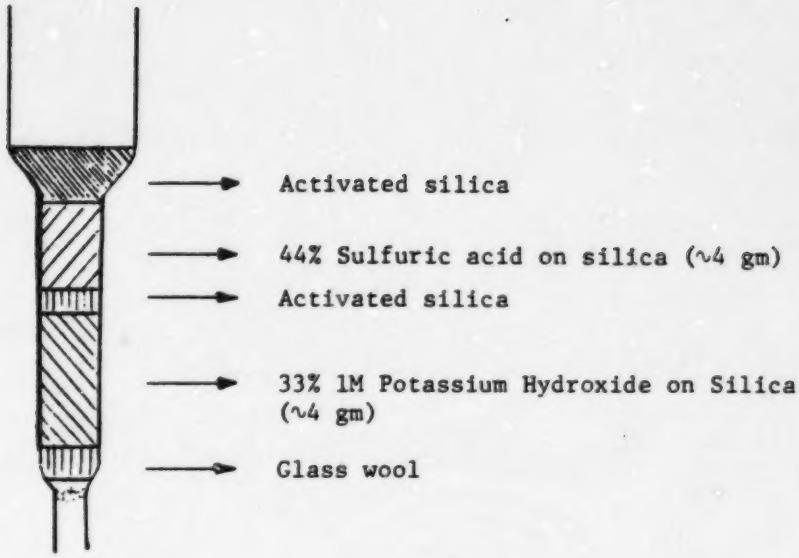

Figure 1. Multilayer silica column for clean-up of extract.

column was eluted with approximately 25 mL of hexane/benzene (1:1) with the entire eluate being collected. The multilayered silica column removed acidic and basic compounds that might have been co-extracted along with the 2,3,7,8-TCDD as well as the easily oxidized materials. Although this step is often accomplished using liquid-liquid washes in a separatory funnel, the multilayered silica column reduces the losses of analyte due to adsorption on glass surfaces and interfacial losses caused by poor separation of the liquid phases as observed both in Battelle and Dow Chemical Laboratories.

The eluate from the multilayered silica column was concentrated using a K-D concentrator and solvent exchanged into 1-2 mL of hexane and added to a second chromatographic column containing approximately 5 g of activated basic alumina. This column was sequentially eluted with 40 mL of hexane, 25 mL of hexane/carbon tetrachloride (1:1), and 20 mL of hexane/methylene chloride (1:1). The hexane/methylene chloride eluate which contained the 2,3,7,8-TCDD was collected and solvent exchanged into 20 uL of n-decane. The n-decane concentrate was stored at 0°C until it was analyzed.

The solvents used, hexane, benzene, carbon tetrachloride, and methylene chloride, were Distilled-in-Glass® (Burdick and Jackson Laboratories, Inc., Muskegon, MI). Alumina and silica gel were purchased from BioRad Laboratories, Richmond, CA. These were solvent rinsed and activated immediately prior to

being used. The 2,3,7,8-tetrachlorodibenzo-p-dioxin-$^{13}C_{12}$ (2,3,7,8-TCDD-$^{13}C_{12}$) was purchased from KOR Isotopes, Cambridge, MA, and the 1,2,3,4-tetrachlorodibenzo-p-dioxin (1,2,3,4-TCDD) was purchased from Ultra Scientific, Inc., Hope, RI. All analytical glassware was washed with soap and water, rinsed with reagent grade acetone, and baked at 450°C for a minimum of 12 hours prior to use.

The XAD-2 precleaned resin, grade number 2-0279 (Supelco, Inc., Bellefonte, PA) was extracted for 18 hours with methylene chloride and dried with a fluidized bed technique prior to being used. Test batches of resin were extracted and blanks checked by glass capillary GC/FID prior to use.

The Florisil was purchased from Sigma Chemical Company, St. Louis, MO, product number F-9217, 60-100 mesh activated at 677°C (1250°F). It was washed with methylene chloride and dried at 400°C prior to use.

INSTRUMENTAL ANALYSIS

The 2,3,7,8-TCDD was quantified in the extracts using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The HRGC system was a Carlo Erba Model 4160 gas chromatograph operated under the following conditions:

Column:	30m DB-5
Carrier Velocity:	30 cm/sec
Starting Temperature:	120°C
Hold Time at Start:	3 min
Program Rate:	20°C/min
Final Temperature:	260°C
Hold Time at Maximum:	9 min
Injection:	splitless, split closed for 45 seconds

The HRMS system was a VG Model MM-7070H high resolution mass spectrometer used under the following conditions:

Electron Ionization:	70 eV
Accelerating Voltage:	4000 volts
Electron Emission:	200 μa
Source Temperature:	200°C
Resolution:	10,000-12,000, M/ΔM, 10% valley

A VG Model 2035 data system capable of controlling the mass spectrometer under high resolution multiple ion detection (HRMID) conditions was used. All data were stored on 9-track magnetic tape and will be retained for five years.

The 2,3,7,8-TCDD levels were quantified by comparing the response of the 2,3,7,8-TCDD with that of the 2,3,7,8-TCDD-$^{13}C_{12}$ using the following equation:

$$\text{2,3,7,8-TCDD (ng)} = \frac{\text{Area of m/z 322}}{\text{Area of m/z 334}} \times \text{ng of 2,3,7,8-TCDD-}^{13}C_{12}$$

QUALITY CONTROL

The HRGC was checked at the start of each day as well as periodically during the course of the analyses. The checks consisted of injecting known quantities of both 2,3,7,8-TCDD and mixed TCDD isomer solutions. These injections served to verify the chromatographic resolution, peak shape, injector liner status, column adsorption, absolute mass spectrometer sensitivity, and correct mass focus of the MID unit. From past experience, variations in these parameters, such as absolute response, can be correlated to specific instrument conditions which need attention.

The HRMS was tuned each day using perfluorokerosene (PFK). The tuning consisted of optimizing the various lens and focus voltages to provide the best sensitivity and peak shape. The resolution was adjusted such that it was between 10,000 and 12,000 (10% valley, M/ΔM definition). The lock mass, for MID control, was m/z 319 for PFK. Its mass focus was verified by the mass marker as well as by manual interpretation. During the analyses its intensity was monitored to assure that sensitivity changes did not occur. Five ion masses were monitored during each analysis. They were:

m/z 318.9792	Mass Spectrometer Lock Mass
m/z 319.8965	Native TCDD
m/z 321.8936	Native TCDD
m/z 331.9368	TCDD-$^{13}C_{12}$
m/z 333.9338	TCDD-$^{13}C_{12}$

The lock mass peak was produced from a low level of PFK which was continuously introduced into the ion source using the batch inlet. The peak was centroided by the data system to provide mass focus correction thus assuring that the TCDD ion masses were accurately monitored. Two native TCDD ion masses and two TCDD-$^{13}C_{12}$ ion masses were monitored to enhance the specificity of the analyses. Although one ion mass from each would be sufficient for quantification (e.g., m/z 320 and m/z 332 or m/z 322 and m/z 334) by monitoring two masses, it is possible to include the isotope ratio as one of the criteria for identifying TCDD.

The criteria used in this program to identify 2,3,7,8-TCDD were the following:

- Retention time must agree with the internal standard within ± 1 sec
- Ratio of m/z 320 to m/z 322 must be 0.77 ± 0.08 (10%) of 77
- Signal to noise ratios for m/z 320 and m/z 322 must be greater than 3/1.

A typical analysis of a 2,3,7,8-TCDD test mixture containing 95 pg/µL of 2,3,7,8-TCDD-$^{13}C_{12}$ and 20 pg/µL of 2,3,7,8-TCDD is shown in Figures 2A, 2B, 2C, and 2D. From this analysis the chromatographic performance was verified and the quantitative accuracy of the system was assessed. For each test mixture that was analyzed the quantity of 2,3,7,8-TCDD present was calculated.

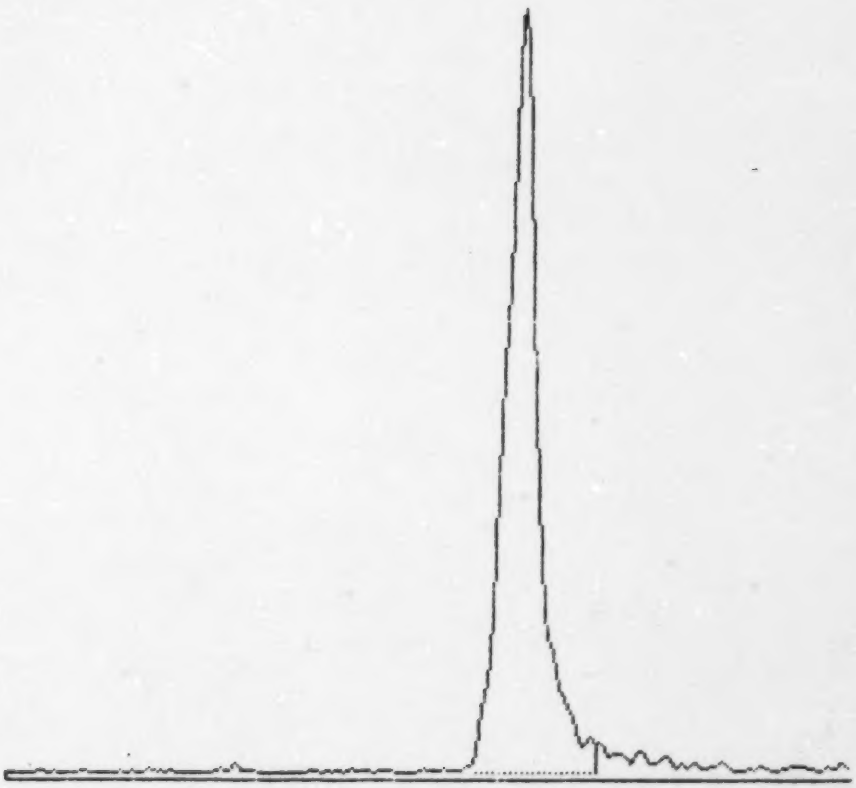

Figure 2A. Trace of m/z 320 in standard test mixture (20 pg 2,3,7,8-TCDD and 95 pg of 2,3,7,8-TCDD-$^{13}C_{12}$.

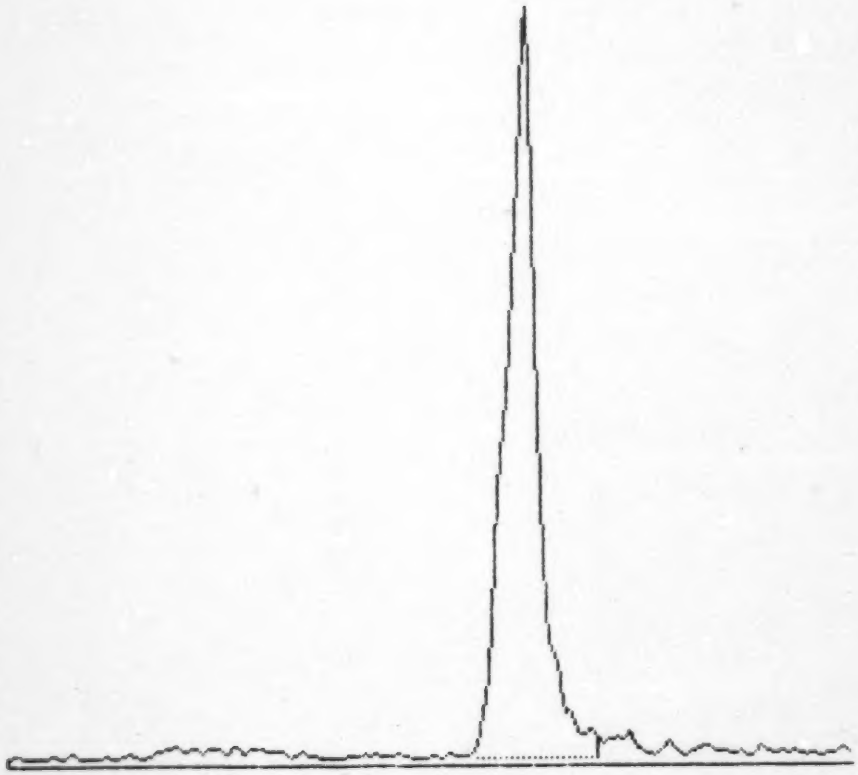

Figure 2B. Trace of m/z 322 in standard test mixture (20 pg 2,3,7,8-TCDD and 95 pg of 2,3,7,8-TCDD-$^{13}C_{12}$.

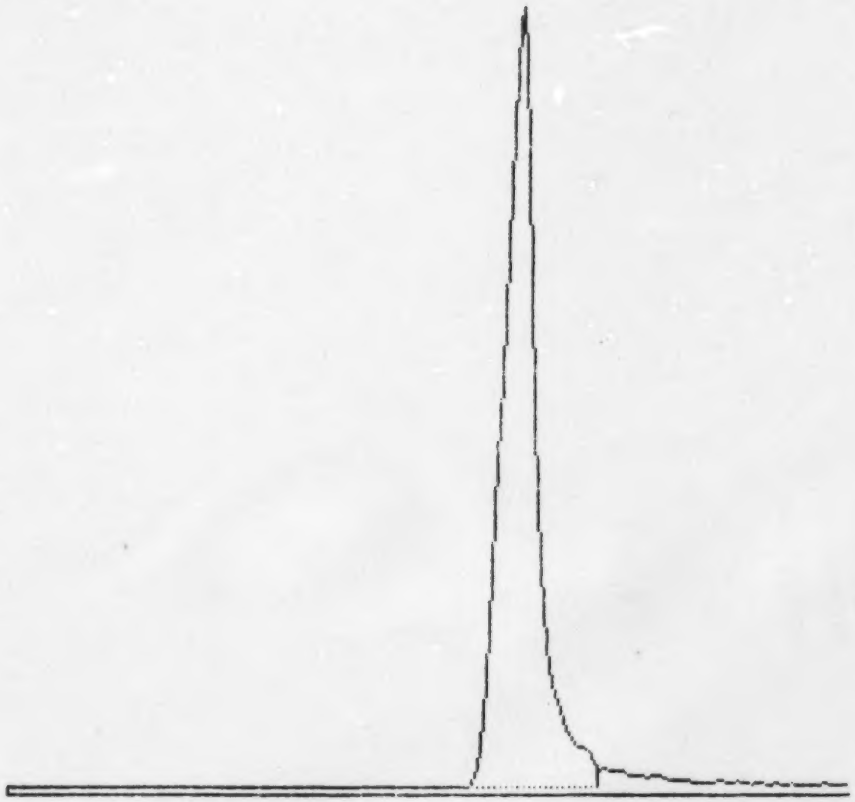

Figure 2C. Trace of m/z 332 in standard test mixture (20 pg 2,3,7,8-TCDD and 95 pg of 2,3,7,8-TCDD-$^{13}C_{12}$.

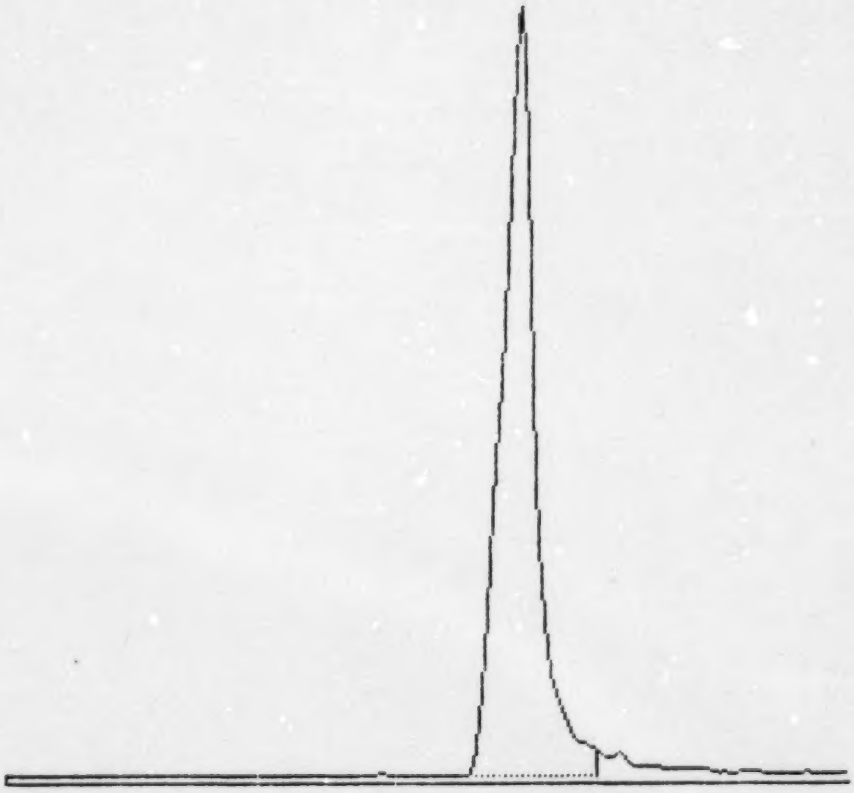

Figure 2D. Trace of m/z 334 in standard test mixture (20 pg 2,3,7,8-TCDD and 95 pg of 2,3,7,8-TCDD-$^{13}C_{12}$.

In addition the ratios of m/z 320/m/z 322 and m/z 332/m/z 334 were also calculated. The quantity of 2,3,7,8-TCDD determined as well as the ion ratios are sensitive to any error in MID mass assignment. Typically the 2,3,7,8-TCDD will quantify to 20 pg ± 3 pg and the ion ratios will compare within ± 0.07 of the theoretical value (0.77).

Method blanks and solvent injections were also analyzed concurrently with the samples. The method blanks served to verify that TCDDs were present in the extraction solvent, liquid chromatography packing material, or elution solvents. The solvent injections were used to determine if any carry over occurred following the analysis of a sample containing 2,3,7,8-TCDD. Solvent injections were made periodically, however, they were always made following a sample which contained relatively high levels of TCDDs as compared to the average of the group.

At the completion for the work assignment, the Battelle QA Officer, Mr. Richard E. Heffelfinger reviewed the completed work and checked for compliance with the QA/QC requirements of the workplan. The results of his audit are summarized in the Task Quality Assurance (QA) Audit report in Appendix A.

SECTION 4

RESULTS AND DISCUSSION

The results of the twenty eight spiking experiments are summarized in Table 2 for XAD-2 resin and Table 3 for Florisil. The 2.1 ng and 16.5 ng levels were the actual determined levels in the spiking solution targeted at 3 ng and 30 ng. The low determined levels are most likely due to decomposition of the 2,3,7,8-TCDD during the storage period or possibly due to adsorption on the surface of the container. In general, the overall percent recovery data from either the XAD-2 resin or Florisil were very good and averaged 92 $\pm$ 8 and 95 $\pm$ 6, respectively. The spiking methods used (A and B) were found to be essentially equivalent with regards to recovery efficiencies. The average percent recovery from XAD-2 resin was 94 $\pm$ 6 when Method A was used and 91 $\pm$ 10 when Method B was used. Likewise, the average percent recovery from Florisil was 102 $\pm$ 6 when Method A was used and 89 $\pm$ 6 when Method B was used. The data obtained in Task 131 Contract Number 68-02-2686 gave comparable results or an overall system recovery of 94 percent.

In general, the data indicate that either Florisil or XAD-2 can be used effectively for sampling 2,3,7,8-TCDD. However, the recovery results appear to be more consistent when XAD-2 resin was used as compared to Florisil. In addition, XAD-2 was shown on many occasions to be a universal adsorber for organics in general[1,2,3] and would therefore be more useful than Florisil if several compounds need to be determined including dioxins.

The reproducibility of the determination as measured by the RSDs (1-12 percent) as well as the recoveries (89-102 percent) of the spiked 2,3,7,8-TCDD indicate that the cleanup and detection procedures described earlier are effective and could be used in sampling and analysis of dioxins.

Methods A and B appear to be equivalent in spiking the dioxin onto the resin with a measurable tendency for lower recoveries when Method B was used. The need for evaporating a larger solvent volume with Method B might explain the possible loss of a very small amount of the dioxin.

TABLE 2. RECOVERY DATA FOR SPIKED NATIVE 2,3,7,8-TCDD ON XAD-2 RESIN

Native Spike Level (ng)	Native Determined Level (ng)			Recovery Percent				RSD	Spiking Method
	Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Rep. 3	Avg.		
0	0.08	ND	ND	ND	ND	ND	ND	ND	A
2.1	2.0	1.8	1.7	95	86	81	87	8	A
16.5	17.4	16.3	15.6	105	99	95	100	5	A
0	0.010	ND	ND	ND	ND	ND	ND	ND	B
2.1	1.8	1.8	2.2	86	86	105	92	12	B
16.5	14.2	14.3	16.0	86	87	97	90/92*	7/8*	B

RSD = Relative standard deviation (percent)
ND = Not determined
* = Overall recovery

TABLE 3. RECOVERY DATA FOR SPIKED NATIVE 2,3,7,8-TCDD ON FLORISIL

Native Spike Level (ng)	Native Determined Level (ng)			Recovery Percent				RSD	Spiking Method
	Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Rep. 3	Avg.		
0	0.017	ND	ND	ND	ND	ND	ND	ND	A
2.1	2.2	2.0	1.8	105	95	86	95	11	A
16.5	17.9	17.8	18.0	108	108	109	108	1	A
0	0.034	ND	ND	ND	ND	ND	ND	ND	B
2.1	1.7	1.7	1.9	81	81	90	84	6	B
16.5	16.8	14.9	15.0	102	90	91	94 95*	7 6*	B

RSD = Relative standard deviation (percent)
ND = Not determined
* = Overall recovery

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2. Characterization of Sorbent Resins for Use in Environmental Sampling, EPA-600/7-78-054 (March 1978).

3. Further Characterization of Sorbents for Environmental Sampling, EPA-600/7-79-216 (September 1979).

APPENDIX A

TASK QUALITY ASSSURANCE (QA) AUDIT

TASK QUALITY ASSURANCE (QA) AUDIT

Date of Audit October 12, 1983

Task No. 008 Contract No. 68-02-3628

Task Title Feasibility of Using Solid Adsorbents for Dioxin Sampling

Task Manager F. L. DeRoos Task Officer M. D. Jackson

Comments:

Applicable Documents: Work Plan & QA Plan Dated February 22, 1983, Laboratory Record Books 37945 & 37534.

Sampling and Sample Tracking: Clearly described - forward tracking excellent.

Analyses--Laboratory Activities: Adequate record of laboratory activities

Results: Program QA plans were adhered to and objectives achieved.

Approved by QA Officer: R. E. Heffelfinger

R. E. Heffelfinger